Chemical Kinetics

This branch of chemistry deals with the study of rates of chemical reactions and the mechanism by which they occur.

While studying reaction rates, one deals with :

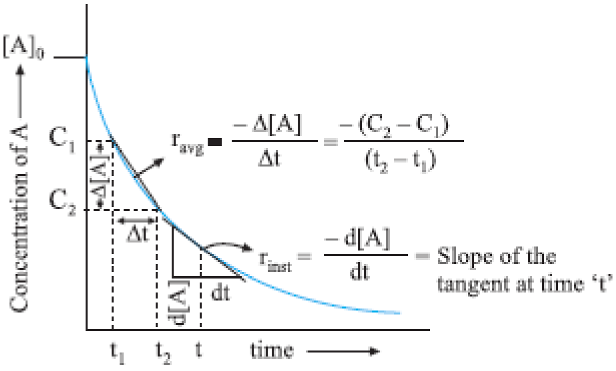
(a) How fast (or slow) the reactants get converted into products

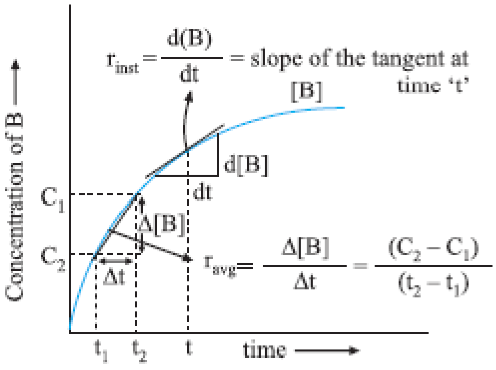
(b) The steps or paths through which the products are formed (*reaction mechanism*)

BASIC Section - 1

Rate of a Reaction :

In general, for a reaction : $A \longrightarrow B$, the behaviour of the concentration of the reactant and product, as the reaction proceeds, is shown graphically.





From the graph, it is clear that the concentration of the reactant decreases and that of the product increases as the reaction proceeds and the rate of the change of the concentration of the reactant as well as that of the product is also changing.

Rate of a reaction can, now, be defined in two ways :

1. Average Rate of reaction (r_{avg}) given by : $r_{avg} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$

where $\Delta[A]$ and $\Delta[B]$ represents the change in the concentrations of ‘A’ and ‘B’ respectively over a time interval Δt.

The average rate of the reaction between a time interval ($t_2 - t_1 = \Delta t$) can be determined from the above graph by locating the concentration of ‘A’ or ‘B’ on this graph at the time instants t_2 and t_1 as shown.
If $[A]_2$ and $[A]_1$ are the concentrations of the reactant ‘A’ at the time instants t_2 and t_1, then :

$$r_{avg} = -\left(\frac{[A]_2 - [A]_1}{t_2 - t_1}\right)$$

Similarly from the plot of 'B' as a function of 't', we have : $r_{avg} = \left(\frac{[B]_2 - [B]_1}{t_2 - t_1}\right)$

Note : The above expressions for r_{avg} is equivalent to the slope of the line joining the points $(t_2, [A]_2)$ and $(t_1, [A]_1)$ or $(t_2, [B]_2)$ and $(t_1, [B]_1)$ as shown.

2. Instantaneous Rate of reaction ($r_{inst.}$) can be calculated from r_{avg} in the limit $\Delta t \longrightarrow 0$ and is represented as :

$$r_{inst} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

Note :

- The above expression for $r_{inst.}$ is equivalent to the slope of the tangent from the plot of the concentration of A' or 'B' at any time instant 't'.
- The rate of the reaction ($r_{inst.}$ or r_{avg}) is always calculated as a positive quantity.
- The rate of the change of the concentration of the reactant will be a negative quantity since its concentration is decreasing with time.
- The rate of the change of the concentration of the product will be a positive quantity since its concentration is increasing with time.
- The magnitude of the rates of the change of the concentration of reactants and products will be equal in this case, as one mole of 'A' gives one mole of 'B' in the above reaction.
- The rate of a reaction at any temperature depends on the concentration of the reactants and sometimes on the concentration of some foreign substances (e.g a catalyst) being used in the reaction as well. The representation of this dependence of the rate of the reaction on the concentrations is known as *rate law* and this *rate law* is determined experimentally.
- The above expression for $r_{inst.}$ is called as differential rate law.

In general for a reaction :

$$mA + nB \longrightarrow pC + qD$$

The rate of reaction can be expressed as follows :

$$\text{Rate} = -\frac{1}{m}\frac{d[A]}{dt} = -\frac{1}{n}\frac{d[B]}{dt} = +\frac{1}{p}\frac{d[C]}{dt} = +\frac{1}{q}\frac{d[D]}{dt}$$

Illustrating the concept :

The rate of formation of NO(g) in the reaction $2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$ *is found to be* 1.6×10^{-4} *M/s. Find the rate of overall reaction and rate of consumption of NOBr.*

We have : $\dfrac{d[NO]}{dt} = 1.6 \times 10^{-4}$ M/s.

Now, Rate of overall reaction $= -\dfrac{1}{2}\dfrac{d[NOBr]}{dt} = +\dfrac{1}{2}\dfrac{d[NO]}{dt} = \dfrac{1}{1}\dfrac{d[Br_2]}{dt} = 0.8 \times 10^{-4}$ M/s

Rate of consumption of NOBr $= \dfrac{d[NOBr]}{dt} = -1.6 \times 10^{-4}$ M/s

Order of a Reaction :

By performing a reaction in actual in laboratory and carefully examining it, it is possible to express the rate law as the product of concentrations of reactants each raised to some power.

For example consider the reaction :

$$P + 2Q \longrightarrow R$$

The differential rate law is written as :

$$\text{Rate} = -\frac{d[P]}{dt} = -\frac{1}{2}\frac{d[Q]}{dt}$$

Also, Rate can be expressed as Rate = $k\,[P]^m\,[Q]^n$

where k is called as rate constant or velocity constant or specific reaction rate.
k is a characteristic of a reaction at a given temperature. It changes only when the temperature changes.

The powers m and n are integers or fractions. m is called as order of reaction with respect to P and n is called as order of reaction with respect to Q.

The overall order of reaction = $m + n$

Note : The values of m and n are calculated from the experimental data obtained for a reaction and the powers m and n are not related to the stoichiometric coefficients of the reactants.

Units of *k* :

In general, the rate law for a n^{th} order reaction can be taken as :

$$\frac{dc}{dt} = -kc^n \qquad \left[\text{Note: } r_{inst.} = -\frac{dc}{dt} = kc^n\right]$$

where k : rate constant ; c : concentration and n : order of reaction

$$\Rightarrow \quad k = \frac{dc/dt}{c^n}$$

$$\Rightarrow \quad \text{Units of } k \equiv (\text{mol/L})^{1-n}\,(\text{time})^{-1}$$

For a 'zero' order reaction (n = 0) :

Units of $k \equiv$ (mol/ L)^1 (time)$^{-1}$

$\Rightarrow$ Units are : mol/L/sec, mol/L/min, ... etc.

For a first order reaction (n = 1) :

Units of $k \equiv$ (time)$^{-1}$

$\Rightarrow$ Units are : sec^{-1}, min^{-1}, hrs^{-1} etc.

For a second order reaction (n = 2) :

Units of $k \equiv$ (mol/ L)$^{-1}$ (time)$^{-1}$

$\Rightarrow$ Units are : L/mol/sec, L/mol/min, ... etc.

Illustration - 1 *From the rate laws for the reactions given below, determine the order with respect to each species and the overall order:*

(i) $2HCrO_4^- + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 8H_2O$
$Rate = k\,[HCrO_4^-][I^-]^2[H^+]^2$

(ii) $H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$
$Rate = k\,[H_2O_2][I^-]$

SOLUTION :

(i) The order of the reaction with respect to [$HCrO_4^-$] is 1; with respect to [I^-] is 2 and with respect to [H^+] is 2. The overall order of the reaction is 1 + 2 + 2 = 5

(ii) The order of the reaction with respect to [H_2O_2] is 1 and with respect to [I^-] is 1. The overall order of the reaction is 1 + 1 = 2

Note :

- In (i) the stoichiometric coefficient of I^- is 6 whereas the power coefficient (n) in the rate law is 2.
- Reaction (i) may not take place in a single step. It may not be possible for all the 22 molecules to be in a state to collide with each other simultaneously. Such a reaction is called a complex reaction.
- A complex reaction takes place in a series of a number of elementary reactions.

Illustration - 2 *For a reaction* $2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$ *; the following data were obtained.*

	[NO](mol/L)	[H_2](mol/L)	Rate(mol/L/s)
1.	5×10^{-3}	2.5×10^{-3}	3×10^{-5}
2.	15×10^{-3}	2.5×10^{-3}	9×10^{-5}
3.	15×10^{-3}	10×10^{-3}	3.6×10^{-4}

(a) *Calculate the order of reaction.*

(b) *Find the rate constant.*

(c) *Find the initial rate if* [NO] = [H_2] = 8.0×10^{-3} M

SOLUTION :

Assuming rate law can be expressed as follows :

rate = $k\,[NO]^x\,[H_2]^y$

By analysing the data :

From observations 1 and 2, we see that $[H_2]$ is constant and when [NO] is tripled, the rate is also tripled.

$\Rightarrow$ rate $(r) \propto [NO]$ $\Rightarrow$ $x = 1$

From observations 2 and 3, we see that [NO] is constant ; when $[H_2]$ is increased four times, the rate also increases four times.

rate $\propto [H_2]$ $\Rightarrow$ $y = 1$

$\Rightarrow$ $r = k\,[NO]\,[H_2O]$

$\Rightarrow$ The order of reaction w.r.t NO and H_2 is 1 and the overall order of reaction is 1 + 1 = 2.

Initial rate = $k\,[NO]\,[H_2] = 2.4 \times (8 \times 10^{-3})^2 = 1.536 \times 10^{-4}$ mol/L/s.

n^{th} ORDER REACTIONS — Section - 2

Zero Order Reactions :

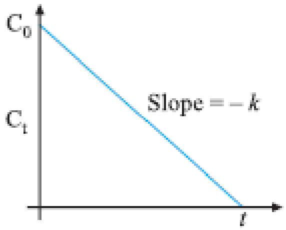
The rate law for zero order reactions ($n = 0$) is written as :

$$\frac{dc}{dt} = -k \qquad \text{.....(i)}$$

Clearly, zero order reactions are those, whose rates are not affected by change in concentrations of reactants (i.e., independent of concentration). The rates of such reactions only depend upon temperature. Most of photochemical reactions are zero order reactions. Other examples are : decomposition of HI over the surface of gold and NH_3 over tungsten.

Equation (i) can be rearranged and integrated to get the variation of the concentration of the reactants as a function of time.

$$\int_{C_0}^{C_t} dc = -\int_0^t k\,dt \quad \Rightarrow \quad [C_t - C_0] = -k\,[t - 0]$$



Thus, $$k = -\frac{[C_t - C_0]}{t} \qquad \text{.....(ii)}$$

where C_0 = Initial concentration of the reactant

and C_t = Concentration of the reactant at any time instant '*t*' after the reaction started

- From the above expression, it is clear that if we plot C_t as a function of time (t) then it will be a straight line with a negative slope = $-k$ and Y– Intercept of $C_{0.}$
- One can also define, Half Life ($t_{1/2}$) which is equal to the time taken for the reactant's concentration to drop to 50% of its initial value.

Putting $C_t = 0.5\, C_0$ in equation (ii), we get $t = t_{1/2} = \dfrac{C_0}{2k}$

Thus, for a Zero order reaction, half life is directly proportional to initial concentration of the reactant.

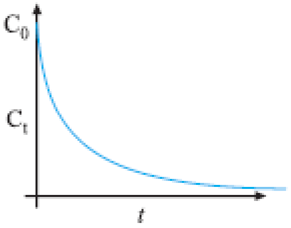
> **Note :** The equation obtained on integrating the differential rate law is known as Integrated Rate Law.
> For example : equation (ii) is the Integrated Rate Law for the Zero Order Reaction.

First Order Reactions :

The differential rate law for a first order reaction A $\longrightarrow$ B; is given as :

$$\frac{dc}{dt} = -k\,c \qquad \text{. . . . .(i)}$$

This equation can be rearranged and integrated as follows to get the *integrated rate law* for a first order reaction :



$$\int_{C_0}^{C_t} \frac{dc}{c} = -\int_0^t k\,dt \quad \Rightarrow \quad \ln\frac{C_0}{C_t} = kt$$

$$\text{or} \qquad 2.303\,\log_{10}\frac{C_0}{C_t} = kt \qquad \text{. . . . .(ii)}$$

[ln is the Natural Log (base 'e') $\equiv \log_e$]

Sometimes, it is important to remember the $\log_{10}$ for the following values :

$\log_{10} 2 = 0.301$ $\quad$ $\log_{10} 3 = 0.477$ $\quad$ $\log_{10} 4 = 0.602$

$\log_{10} 5 = 0.699$ $\quad$ $\log_{10} 6 = 0.778$ $\quad$ $\log_{10} 7 = 0.845$

Also, remember that $\ln x \equiv \log_e x = 2.303 \log_{10} x$

Putting $C_t = 0.5\, C_0$ in equation (ii), we get $t = t_{1/2} \dfrac{2.303 \log_{10} 2}{k} = \dfrac{0.693}{k}$

Thus, for a first order reaction half life is independent of the initial concentration of the reactant.

For the reaction	A	$\longrightarrow$	B	(following first order)
Initial conc.	C_0		0	
After time 't'	$C_t \equiv C_0 - x$		x	

The integrated rate law can also be written as :

$$2.303\log_{10}\frac{C_0}{C_0-x}=kt \qquad \text{or} \qquad 2.303\log_{10}\frac{1}{1-\alpha}=kt$$

where x is the concentration of the reactant consumed and α is the degree of dissociation $=\frac{x}{C_0}$

Features of a First Order Reaction :

1. A first order reaction must follow above form of rate law for all time instants.
This means if we are given value of C_0 and values of x at different time instants [i.e $(C_0 - x)$ as value of reactants after t], the values of k can be calculated for different time instants by using the above first order law. If the reaction for which the data were given is a first order reaction, then all values of k will approximately equal to each other.

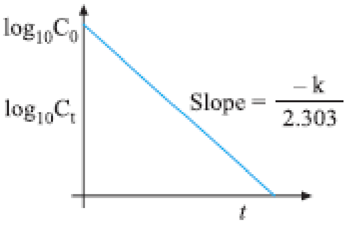
2. The time for half reaction for a first order reaction is independent of initial concentration of reactants.

3. The concentration of reactants in a first order reaction decreases exponentially with time (see figure) $[C_t = C_0e^{-kt}$ from (ii)]

Note that plot of $\log_{10} C_t$ vs t is linear. It is important to note that equation of this straight line is of the form :

$y = mx + b$. Comparing it with Ist order rate law as follows :

$$kt = 2.303\ \log_{10}\frac{C_0}{C_t}$$



$$\Rightarrow \quad \log_{10}C_t=\left(\frac{-k}{2.303}\right)t+\log_{10}C_0 \text{ is the equation of line.}$$

Note that slope of the line $=\left(\frac{-k}{2.303}\right)$ and Y-intercept (OA) $= \log_{10} C_0$

- Rate constant of a first order reaction can also be calculated by measuring the concentration of the reactant at two time instants (if the initial concentration is not known).

  If C_1 and C_2 are the reactant's concentrations at two time instants 't_1' and 't_2' respectively, then we have :

$$2.303\,\log_{10}\frac{C_0}{C_1} = kt_1 \qquad \text{.....(iii)}$$

and $$2.303\,\log_{10}\frac{C_0}{C_2} = kt_2 \qquad \text{.....(iv)}$$

Subtracting (iv) from (iii), we get :

$$2.303\,\log_{10}\frac{C_1}{C_2} = k\left(t_2 - t_1\right)$$ Thus, *k* can be evaluated.

- After Ist half life : $C_t = C_0/2$ ⇒ $\frac{C_t}{C_0} = \frac{1}{2}$

After 2nd half life : $C_t = C_0/2^2$ ⇒ $\frac{C_t}{C_0} = \left(\frac{1}{2}\right)^2$

⇒ After nth half life : $\frac{C_t}{C_0} = \left(\frac{1}{2}\right)^n$ (where $n = t/t_{1/2}$ = No. of half lives)

Note : The differential rate law can be integrated for a nth order reaction as follows :

Using : $\frac{dc}{dt} = -k\,c^n$ [Provided that all the reactants are present in the same molar concentrations]

$$\Rightarrow \int_{C_0}^{C_t}\frac{dc}{c^n} = -\int_0^t k\,dt \quad \Rightarrow \quad \frac{1}{(n-1)}\left[\frac{1}{C_t^{n-1}} - \frac{1}{C_0^{n-1}}\right] = kt \qquad \text{.....(v)}$$

The above equation is the integrated rate law for a nth order reaction.

Also, linear plot can be obtained for $1/c_t^{n-1}$ vs t. $(n \neq 1)$

Putting $C_t = 0.5C_0$ in equation (v), we get $t = t_{1/2} = \frac{1}{(n-1)\,C_0^{n-1}\,k}\left[2^{n-1} - 1\right]$ .....(vi)

From the above expression, it is clear that $t_{1/2} \propto \frac{1}{C_0^{n-1}}$

Order of a reaction (n) can also be obtained by measuring the half life ($t_{1/2}$) of a reaction at different values of initial concentration (C_0) of the reactant molecules.

- If C_{01}, C_{02} are the initial concentrations of the reactants and $(t_{1/2})_1$, $(t_{1/2})_2$ are the corresponding half lives, then using (vi), we get :

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{C_{02}}{C_{01}}\right)^{n-1}$$

Taking log on both sides, we get : $$n = 1 + \frac{\log_{10} \dfrac{(t_{1/2})_1}{(t_{1/2})_2}}{\log_{10}\left(\dfrac{C_{02}}{C_{01}}\right)}$$

Illustration - 3 *The half life of first order decomposition of nitramide is* 2.1 *hour at* 15°*C.*

$$NH_2NO_2\,(aq) \longrightarrow N_2O(g) + H_2O(l)$$

If 6.2 *gm of* NH_2NO_2 *is allowed to decompose, find :*

(a) *time taken for nitramide to decompose* 99%

(b) *volume of dry* N_2O *gas produced at this point at STP.*

SOLUTION :

(a) Using first order kinetics, we have :

$$kt = 2.303 \log_{10} \frac{C_0}{C_t}$$

$$\Rightarrow \quad \frac{0.693}{2.1} \times t = 2.303 \log_{10}\left(\frac{100}{00-99}\right) \quad \left[\because k = \frac{0.693}{t_{1/2}}\right] \quad \Rightarrow \quad t = 13.96 \text{ hours}$$

(b) 6.2 gm of $NH_2NO_2 \equiv 0.1$ mol

	$NH_2NO_2(aq.) \longrightarrow$	$N_2O(g) + H_2O(\ell)$
Moles at t = 0	0.1 mol	
Moles at t = 13.96 hrs	$0.1 - 0.99 \times 0.1$	0.99×0.1

$\Rightarrow$ Moles $N_2O = 0.099$

$\Rightarrow$ V_{N_2O} at STP $= 0.099 \times 22.4$ L $= 2.217$ L at STP

Molecularity

As already discussed, the order of a reaction is an experimental concept. The theoretical aspect of chemical kinetics is molecularity.

A complex chemical reaction is understood in terms of various indirect steps called elementary processes. The study of a reaction in terms of elementary processes is called as reaction mechanism. Now various elementary steps occur at different rates. The slowest elementary process in the reaction mechanism is called as rate determining step.

Molecularity is defined as the number of ions or molecules or atoms taking part in an *elementary process* of the reaction mechanism.

In the rate determining step, when one molecule takes part, it is said to be a unimolecular reaction ; two molecules take part, it is said to be a bimolecular reaction ; three molecules take part, it is said to be a termolecular reaction.

Unimolecular :

1. Cyclopropane $\longrightarrow$ propene

2. $O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$

3. $N_2O_5\,(g) \longrightarrow N_2O_4\,(g) + 1/2\,O_2\,(g)$

Bimolecular :

1. $NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)$

2. $2HI\,(g) \longrightarrow H_2\,(g) + I_2\,(g)$

Termolecular :

1. $2\,NO\,(g) + O_2\,(g) \longrightarrow 2\,NO_2\,(g)$

Note :

- For a reaction : $A \longrightarrow B$ in the rate law : $\text{rate} = k\,[A]^m\,[B]^n$

  Neither the order of reaction (m + n) nor the molecularity of a reaction can be predicted from stoichiometric coefficient of a balanced reaction. The order of reaction is always to be determined experimentally and molecularity is determined theoretically after studying the reaction mechanism. However as a theoretical idea sometime, we can have an approximate order of reaction equal to molecularity (i.e., the number of molecules taking part in slowest elementary step for complex reactions).

- Order of a reaction can be fraction also. For example consider the following reaction:

  (i) $H_2\,(g) + Br_2\,(g) \longrightarrow 2\,HBr\,(g)$

  $\text{rate} = k\,[H_2]\,[Br_2]^{1/2}$ (determined experimentally)

  $$\text{order of reaction} = 1 + \frac{1}{2} = \frac{3}{2}$$

(ii) $CH_3CHO\ (g) \rightarrow CH_4\ (g) + CO\ (g)$

rate = k $[CH_3CHO]^{3/2}$ (determined experimentally)

order of reaction $= \dfrac{3}{2}$

Also note that sum of stoichiometric coefficient (1 + 1 = 2) is not equal to the order of reaction.

Pseudo First Order Reactions :

The molecularity of acidic hydrolysis of sucrose and esters is 2, whereas their order is 1. In both the reactions water is in excess so that its concentration remains constant throughout the reaction. The rate of reaction therefore depends only on the concentration of sucrose and ester in two reactions respectively. So the reactions in which the molecularity is 2 or 3 but they conform to the first order kinetics are known as *pseudo first order reactions* OR *pseudo unimolecular reactions.*

$$C_{12}H_{22}O_{11} + H_2O + H^+ \longrightarrow C_6H_{12}O_6\ \text{(glucose)} + C_6H_{12}O_6\ \text{(fructose)}$$

$$CH_3COOC_2H_5\ \text{(ester)} + H_2O + H^+ \longrightarrow CH_3COOH + C_2H_5OH$$

(*In both the reactions,* H^+ *ion acts as a catalyst*)

Illustration - 4 *The rate law for the decomposition of gaseous* N_2O_5,

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2\,(g) \text{ is observed to be : } r = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

A reaction mechanism which has been suggested to be consistent with this rate law is

$$N_2O_5(g) \overset{K_{eq}}{\rightleftharpoons} NO_2(g) + NO_3(g) \qquad \text{(fast equilibrium)}$$

$$NO_2(g) + NO_3(g) \xrightarrow{k_1} NO_2(g) + NO(g) + O_2\,(g) \qquad \text{(slow)}$$

$$NO(g) + NO_3(g) \xrightarrow{k_2} 2NO_2(g) \qquad \text{(fast)}$$

Show that the mechanism is consistent with the observed rate law.

SOLUTION :

$r = k_1\ [NO_2]\ [NO_3]$ .....**(i)**

and from the fast equilibrium step,

$$K_{eq} = \frac{[NO_2][NO_3]}{[N_2O_5]}$$

Thus, $[NO_2]\ [NO_3] = K\ [N_2O_5]$ .....**(ii)**

Using (ii) in (i), we get :

$$r = k_1K_{eq}\,[N_2O_5] = k\,[N_2O_5] \qquad \text{where } k = k_1\,K_{eq}$$

This shows that the mechanism is consistent with the observed rate law.

Illustration - 5 *The termolecular reaction* $2NO(g) + H_2(g) \longrightarrow 2NOH(g)$ *is found to be third-order obeying the rate law* $r = k[NO]^2[H_2]$. *Show that it is consistent with either of the following mechanisms :*

(i) $2NO\,(g) \xrightleftharpoons{K_{eq}} N_2O_2\,(g)$ (*fast equilibrium*)

$N_2O_2\,(g) + H_2\,(g) \xrightarrow{k'} 2NOH\,(g)$ (*slow*)

(ii) $2NO\,(g) + H_2\,(g) \xrightleftharpoons{K'_{eq}} NOH_2\,(g)$ (*fast equilibrium*)

$NOH_2\,(g) + NO\,(g) \xrightarrow{k''} 2NOH\,(g)$ (*slow*)

SOLUTION :

(i) Since the slow step is the rate determining step, hence

$$r = k'\,[N_2O_2]\,[H_2]$$

and from the fast equilibrium step,

$$K_{eq} = \frac{[N_2O_2]}{[NO]^2} \qquad \text{or} \qquad [N_2O_2] = K_{eq}\,[NO]^2$$

$$\Rightarrow \qquad r = k'\,K_{eq}\,[NO]^2\,[H_2] = k\,[NO]^2\,[H_2] \qquad \text{where } k = k'K_{eq}$$

(ii) Proceeding as in (i) above, we have

$$r = k''\,[NOH_2]\,[NO]$$

and from the fast equilibrium step,

$$K'_{eq} = \frac{[NOH_2]}{[NO][H_2]} \qquad \text{or} \quad [NOH_2] = K'_{eq}\,[NO][H_2]$$

$$\Rightarrow \qquad r = k''K'_{eq}\,[NO]^2\,[H_2] = k\,[NO]^2\,[H_2] \qquad \text{where } k = k''K'_{eq}$$

Methods of determining the order of a reaction

The following methods are commonly used for determining the order of a reaction :

1. Use of differential rate expressions :

We know that for an n^th^ order reaction, $r = k\, c^n$

Taking log on both sides, we have : $\log_{10} r = \log_{10} k + n \log_{10} c$

Thus, if we plot $\log_{10} r$ as a function of $\log_{10} c$, it should be a straight line with a slope 'n'.

$\Rightarrow$ The order of the reaction can be evaluated.

2. Use of integrated rate laws :

This method can be used both analytically and graphically.

In the analytical method, a certain order of the reaction is assumed and rate constant of the reaction is calculated from the given date. The constancy of the 'k' values obtained suggests that the assumed order of the reaction is correct. If not, we assume a different order for the reaction and again calculate the values of 'k' using the new rate expression. This is essentially a *trial and error method*.

In the graphical method, if the plot of log c versus t is a straight line then the reaction is of first order. Similarly, the integrated expression for second order can be utilized to ascertain if the reaction order is 2 and so on.

3. Half life method :

Provided that all the reactants are present in the same molar concentrations, we have already derived the expression for calculating the order of a reaction given by :

$$n = 1 + \frac{\log_{10} \dfrac{(t_{1/2})_1}{(t_{1/2})_2}}{\log_{10} \left(\dfrac{C_{02}}{C_{01}}\right)}$$

where C_{01}, C_{02} are the initial concentrations of the reactants and $(t_{1/2})_1$, $(t_{1/2})_2$ are the corresponding half lives

4. Isolation method :

Sometimes, the kinetics of a reaction are studied in successive experiments by keeping the concentrations of all but one reactant in excess so that the result gives the order with respect to the reactant whose concentration is changing significantly. The synthesis of HI (g) from H_2 (g) and I_2 (g) is pseudo first order with respect to H_2 (g) in the presence of large excess of I_2 (g) and also pseudo first order with respect to I_2 (g) in the presence of large excess of H_2 (g). Hence, overall the reaction is of second order.

ANALYSIS OF SOME IMPORTANT FIRST-ORDER REACTIONS Section - 3

Analysis of some important first-order reactions :

1. Decomposition of Hydrogen peroxide (H_2O_2)

$$2\,H_2O_2(\ell)\longrightarrow 2\,H_2O(\ell)+O_2(g)$$

The rate of this first order reaction is measured by titrating a fixed volume of H_2O_2 (undecomposed) against a standard solution of $KMnO_4$. Here $KMnO_4$ acts as *oxidising agent* and H_2O_2 as *reducing agent*. The volumes of $KMnO_4$ used for H_2O_2 after regular intervals of time are as follows.

Time instants	t = 0	t_1	t_2	t_3	t_4	t_5
Vol. of $KMnO_4$	V_0	V_1	V_2	V_3	V_4	V_5

Volume of $KMnO_4$ at t = 0 corresponds to volume of H_2O_2 initially present. $\Rightarrow$ $C_0 \propto V_0$

Volume of $KMnO_4$ at time instants $t_1, t_2, t_3, \ldots$ corresponds to volume of H_2O_2 remaining after $t_1, t_2, t_3, \ldots$ $\Rightarrow$ $C_t \propto V_t$

Now it being a first order reaction, follows first order kinetics, so $kt = 2.303 \log_{10} \dfrac{V_0}{V_t}$

Now using the above expression, if we calculate the values of k for different time intervals $t_1, t_2, \ldots$ (for actual numerical data), the values of k should be same if the reaction follows first order kinetics.

2. Decomposition of ammonium nitrite (NH_4NO_2) and benzene diazonium chloride ($C_6H_5N{=}NCl$)

$$NH_4NO_2(s)\longrightarrow 2\,H_2O(\ell)+N_2(g)$$

$$C_6H_5-N=N-Cl(\ell)\longrightarrow C_6H_5-Cl(\ell)+N_2(g)$$

The rate of both the reaction is studied (measured) in similar manner. The volume of nitrogen (N_2) is collected after a regular interval of time as follows :

Time instants	t = 0	t_1	t_2	t_3	t_4	t
Vol. of N_2	0	V_1	V_2	V_3	V_4	V_t

At t = 0, clearly the volume of $N_2 = 0$

Time instant $t = \infty$ means the end of a reaction i.e., when whole of NH_4NO_2 or $C_6H_5-N=N-Cl$ is decomposed.

$\Rightarrow$ At $t = \infty$, V_∞ corresponds to the initial volume of NH_4NO_2 or $C_6H_5 - N = N - Cl$.

(Note that the ratio of stoichiometric coefficient for both $N_2 : NH_4NO_2$ or $N_2 : C_6H_5N = NCl$ is 1 : 1).

$\Rightarrow \quad C_0 \propto V_\infty$

At $t = t_1, t_2, t_3, \ldots$, the volume of N_2 corresponds to concentration of product formed i.e., equal to x.

$\Rightarrow \quad x \propto V_t$

$\Rightarrow \quad C_0 - x \propto V_\infty - V_t \quad \Rightarrow \quad kt = 2.303 \log_{10} \dfrac{V_\infty}{V_\infty - V_t}$

3. Hydrolysis of esters ($CH_3COOC_2H_5$)

$$CH_3COOC_2H_5 \text{ (ester)} + H_2O + HCl\,(H^+) \longrightarrow CH_3COOH + C_2H_5OH$$

The reaction rate is measured by titrating the acid (CH_3COOH) produced against a standard alkali solution. Note that when a test sample is prepared from the reacting mixture, there are two acids : one is mineral acid H^+ (HCl or any other) and second is CH_3COOH produced. So volume of alkali used gives titration value for both acids. The data is collected in the following manner.

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_∞
Vol. of NaOH	V_0	V_1	V_2	V_3	V_4	V_∞

At $t = 0$, V_0 is the volume NaOH used to neutralise the mineral acid present (H^+) being used as catalyst. (At $t = 0$, *no* CH_3COOH *is yet produced*)

At $t = \infty$ (i.e. at the end of hydrolysis), V_∞ is the volume of NaOH used to neutralise whole of CH_3COOH *plus* vol. of HCl present. At $t = \infty$, volume of CH_3COOH corresponds to volume of ester taken initially.

$\Rightarrow \quad C_0 \propto V_\infty - V_0 \qquad$ (as $V_0 \equiv$ vol. of HCl)

At $t = t_1, t_2, t_3, \ldots$, $V_1, V_2, V_3, \ldots$ corresponds to vol. of HCl *plus* vol. of CH_3COOH being produced.

$\Rightarrow \quad x \propto V_t - V_0$

$\Rightarrow \quad C_0 - x \propto (V_\infty - V_0) - (V_t - V_0) \qquad \Rightarrow \qquad C_0 - x \propto V_\infty - V_t$

$\Rightarrow \quad kt = 2.303 \log 10 \dfrac{V_\infty - V_0}{V_\infty - V_t}$

4. Kinetics of some reactions can be studied by measuring optical rotation of reaction mixture at different interval of time.

(i) Inversion of Cane Sugar ($C_{12}H_{22}O_{11}$)

$$C_{12}H_{22}O_{11} + H_2O + H^+ \longrightarrow C_6H_{12}O_6\ \text{(glucose)} + C_6H_{12}O_6\ \text{(fructose)}$$

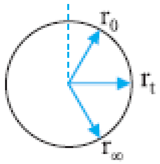
The rate is measured by measuring the change in the angle of rotation (optical activity) by a polarimeter. Sucrose is *dextro-rotatory*, glucose is *dextro-rotatory* and fructose is *leavo-rotatory*. The change produced in rotatory power in time *t* gives a measure of *x*, the quantity of sucrose decomposed in that time. The total change in the rotatory power produced at the end of the reaction gives the measure of C_0, the initial concentration of sucrose.

If r_0, r_t and r_∞ represent rotations at the start of reaction, after time t and at the end of reaction respectively, then

$$\Rightarrow \quad C_0 \propto r_0 - r_\infty \qquad \text{and} \qquad x \propto r_0 - r_t$$

$$\Rightarrow \quad C_0 - x \propto r_t - r_\infty$$

$$\Rightarrow \quad kt = 2.303 \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$



(ii) Consider the following first order reaction on which A, B and C are optically active compounds which rotate the place polarized light in the clockwise or anticlockwise direction.

$$A(\text{soln.}) \rightarrow B(\text{soln.}) + C(\text{soln.})$$

Time	0	t	∞
Total rotation in degrees	r_0	r_t	r_∞

Let the specific optical rotations of A, B and C per unit concentration be, r_a, r_b and r_c (including +ve or –ve sign).

Let the initial concentration of A be C_0 and the decrease in concentration till time t be x.

$$A(\text{soln.}) \rightarrow B(\text{soln.}) + C(\text{soln.})$$

At time = 0	C_0	0	0
At time = t	$C_0 - x$	x	x
At time = ∞	0	C_0	C_0

Such that $\quad k = \frac{1}{t}\,\text{In}\,\frac{Co}{Co - x}$

Optical rotation at time = 0, $\quad r_a C_0 = r_0$ **....(i)**

Optical rotation at time = t, $\quad r_a(C_0 - x) + x\,r_b + x\,r_c = r_t$.

$$r_a C_0 + x(r_b + r_c - r_a) = r_t$$

$$r_0 + x(r_b + r_c - r_a) = r_t \qquad \text{....(ii)}$$

Optical rotation at time $= \infty$, $\quad C_0(r_b + r_c) = r_\infty \qquad$ **....(iii)**

From equation (ii)

$$x = \frac{r_t - r_0}{(r_b + r_c - r_a)} \qquad \text{....(iv)}$$

Since constant involved in x is $\frac{1}{(r_b + r_c - r_a)}$, the same constant must appear in expression of C_0 .

Thus, subtracting equation (i) from equation (iv), we get :

$$C_0 = \frac{r_\infty - r_0}{(r_b + r_c - r_a)} \qquad \text{....(v)}$$

Subtracting equation (iv) from equation (v)

$$C_0 - x = \frac{r_\infty - r_1}{(r_b + r_c - r_a)}$$

$$\therefore \qquad k = \frac{1}{t} \ln \frac{r_\infty - r_0}{r_\infty - r_t}$$

5. In first-order reactions involving gases, sometime measuring the pressure of the reaction mixture is very good method for measuring reaction rates.

For example consider decomposition of arsine gas (AsH_3).

$$AsH_3\,(g) \longrightarrow As\,(s) + \frac{3}{2} H_2\,(g)$$

The rate of reaction is measured as the *increase* in pressure of the reaction mixture. Note that there is an increase in number of moles of the gaseous products to the right, so as the reaction proceeds, there will be an increase in pressure of contents ($P \propto n$).

Let the initial pressure of AsH_3(g) is P_0, if x is the decrease in pressure of AsH_3(g) after time t.

	$AsH_3(g)$	$\longrightarrow$	As (s)	+	$\frac{3}{2}H_2(g)$
$C_0 \equiv$ initial pressure	P_0		0		0
$C_t \equiv$ partial pressure	$P_0 - x$		0		$\frac{3}{2}x$

Arsenic is solid, so P(As) = 0

After time t, let P_t be the total pressure, then

$$P_t = P(AsH_3) + P(H_2) = (P_0 - x) + \frac{3x}{2}$$

$$\Rightarrow \quad P_t = P_0 + \frac{x}{2} \qquad \Rightarrow \qquad x = 2\,(P_t - P_0)$$

Now $C_0 \propto P_0$

and $C_t \propto P_0 - x \equiv P_0 - 2\,(P_t - P_0) \equiv 3P_0 - 2P_t \quad \Rightarrow \quad kt = 2.303 \log_{10} \frac{P_0}{3P_0 - 2P_t}$

On similar pattern, please try to write the expression for Ist order rate law for following first-order reactions. (in terms of P_o and P_t)

1. $N_2O(g) \longrightarrow N_2(g) + \frac{1}{2} O_2(g)$
2. $(CH_3)_3C - O - O - C(CH_3)_3\,(g) \longrightarrow 2\,(CH_3)_2C = O(g) + C_2H_6(g)$

ACTIVATION ENERGY (E_a) Section - 4

A mixture of magnesium and oxygen does not react at room temperature. But if a burning splinter is introduced to the mixture, it burns vigorously. Similarly a mixture of methane and oxygen does not react at room temperature, but if a burning match-stick is put in the mixture, it burns rapidly. *Why it happen like this, that some external agents has to be introduced in order to initiate the reaction* ?

According to the theory of reaction rates " *for a chemical reaction to take place, reactant molecules must make collisions among themselves* ". Now in actual, only a fraction of collisions are responsible for the formation of products, i.e., not all collisions are *effective* enough to give products. So the collisions among reactant molecules are divided into two categories :

Effective collisions and *In-effective collisions*

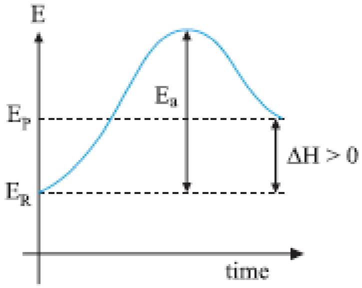
Effective collisions are collisions between the molecules which have energies equal to or above a certain minimum value. This minimum energy which must be possessed by the molecules in order to make an effective collision (i.e., to give a molecule of products) is called as *threshold energy*. So it is the effective collisions which bring about the occurrence of a chemical reaction.

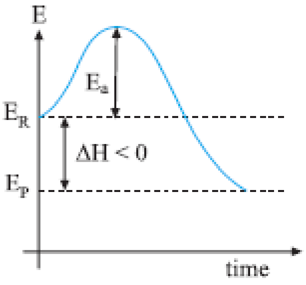
Ineffective collisions are the collisions between the molecules which does not posses the *threshold energy*. These can not result in a chemical reaction.

Now most of the times, the molecules of reactants do not possess the threshold energy. So in order to make effective collisions (i.e., to bring about the chemical reaction), an additional energy is needed to be absorbed by the reactant molecules. This additional energy which is absorbed by the molecules so that they achieve the threshold energy is called as *energy of activation* or simply *activation energy*. It is represented as E_a.

Note :

- The progress of the reaction can studied in a graph with energy of the reacting system. You can find ΔH and E_a from graph below.
- All the colliding molecules must collide at a proper orientation for a collision to be effective, other than "sufficient energy" factor. A reaction having more number of reactants (high molecularity) is expected to be slower because it is less probable that all the reactant molecules, with energy greater than activation energy collide simultaneously at proper orientation.





A reaction which needs higher activation energy is slow at a given temperature.

For example : $NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$ is faster at ordinary temperature whereas the following reaction :

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ is slower at the same temperature as the value of E_a for the second reaction is much higher.

Arrhenius Equation :

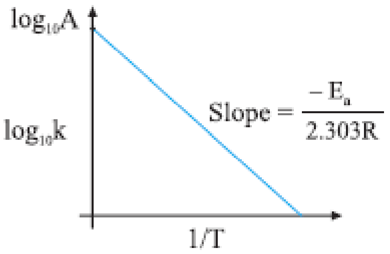
Arrhenius proposed the following equation for the determination of activation energy (E_a) at a given temperature T.

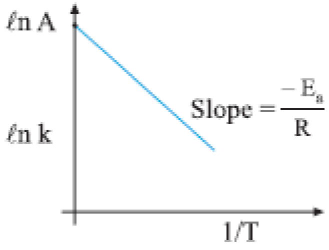
$$k \propto e^{-E_a/RT} \qquad \Rightarrow \qquad k = A\,e^{-E_a/RT}$$

where E_a = activation energy, A = frequency factor and k = rate constant

Simplifying the equation :

$$\log_{10} k = \frac{-E_a}{2.303\,RT} + \log_{10} A$$

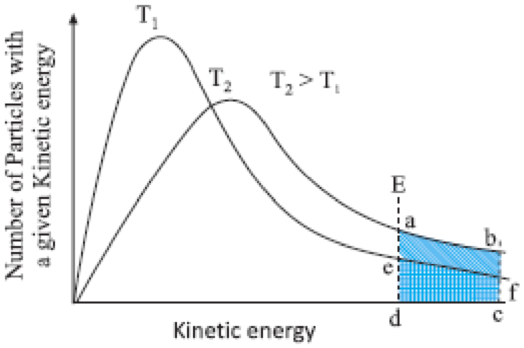




Now a plot of $\log_{10} k$ or $\ell n k$ vs 1/T will be a straight line whose equation is given above. If k_1 is the value of the rate constant at T_1 K and k_2 is the value of rate constant at T_2 K for a reaction whose energy of activation is E_a, then

$$\left.\begin{aligned} k_1 &= A\,e^{-Ea/RT_1} \\ \text{and}\quad k_2 &= A\,e^{-Ea/RT_2} \end{aligned}\right\} \text{Divide and take } \log_e \text{ on both sides to get : } \log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303RT}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

This equation is called as *Integrated Arrhenius equation*. This equation is very useful in determining the value of E_a of a reaction by knowing the values of k_1 and k_2 at different temperatures T_1 and T_2.



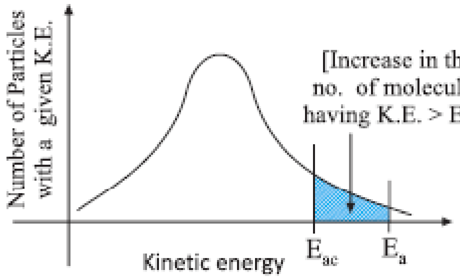
Note :

- For most of the reactions, a 10° C rise near the room temperature, the rate constant is almost doubled i.e. $\frac{k_{35°C}}{k_{25°C}} \approx 2$.

  This can be explained by the fact that the number of molecules possessing energy greater than the *threshold energy* increases tremendously as shown by the shaded area (a–b–f–e–a) in the figure.
- The fraction of molecules having internal energy greater than or equal to E_a is equal to $e^{-E_a/RT}$. This shows that as temperature increases, the number of molecules crossing this energy barrier increases tremendously, accounting for the increase in the rate constant.

- Rate constant ‘k’ can also be increased by reducing ‘E_a’ to ‘E_{ac}’ through the addition of a catalyst in the system.

$$k_1 = Ae^{-E_a/RT} \text{ and } k_2 = Ae^{-E_{ac}/RT}$$



$$\Rightarrow \qquad \log_{10}\frac{k_2}{k_1} = \frac{E_a - E_{ac}}{2.303RT}$$

Note : $$\log_{10}\frac{(k_2)_f}{(k_1)_f} = \frac{(E_a)_f - (E_{ac})_f}{2.303RT} \qquad \text{....(i)}$$

and $$\log_{10}\frac{(k_2)_b}{(k_1)_b} = \frac{(E_a)_b - (E_{ac})_b}{2.303RT} \qquad \text{....(ii)}$$

$$\log_{10}\frac{(k_2)_f}{(k_1)_f} = \frac{(E_a)_f}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{....(iii)}$$

$$\log_{10}\frac{(k_2)_b}{(k_1)_b} = \frac{(E_a)_b}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{....(iv)}$$

where $(E_a)_f$ and $(E_a)_b$ are the activation energies of the reaction in forward and backward reaction, and $(E_{ac})_f$ and $(E_{ac})_b$ are the activation energies of catalysed reaction in forward and backword reaction.

Illustration - 6 *The activation energy of the reaction : $A + B \longrightarrow$ products is* 105.73 *kJ/mol. At* 40°*C, the products are formed at the rate of* 0.133 *mol/L/min. What will be rate of formation of products at* 80°*C* ?

SOLUTION :

Let the rate law be defined as

At T_1 : $r_1 = k_1 [A]^x [B]^y$

At T_2 : $r_2 = k_2 [A]^x [B]^y$

$$\Rightarrow \quad r_2 = r_1\left(\frac{k_2}{k_1}\right)$$

Using Arrhenius equation, find k at 40°C.

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1\,T_2}\right)$$

$$\Rightarrow \quad \log_{10}\frac{k_2}{k_1}=\frac{105.73\times10^3}{2.303\times8.31}\left(\frac{40}{313\times353}\right)$$

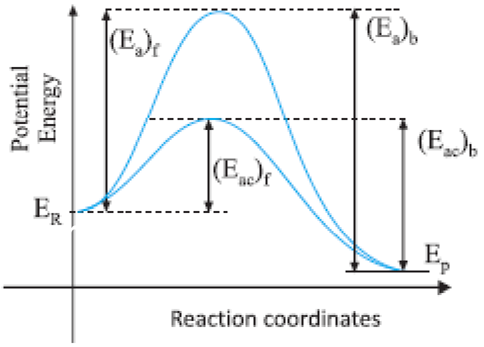
$$\Rightarrow \quad \frac{k_2}{k_1}=2.0$$

$$\Rightarrow \quad \frac{k_2}{k_1}=100$$

$$\Rightarrow \quad r_2 = 0.133\times100 = 13.3 \text{ mol/L/min}$$

Illustration - 7 *The activation energy of a non–catalysed reaction at* 37°*C is* 200 *kcal/mol and the activation energy of the same reaction when catalysed decreases to only* 60.0 *kcal/mol. Calculate the ratio of rate constants of the two reactions.*

SOLUTION :



$$\Rightarrow \quad \log_{10}\frac{k_c}{k}=\frac{1}{2.303\,R\,T}\left(E_a-E_{ac}\right)$$

$$\Rightarrow \quad \log_{10}\frac{k_c}{k}=\frac{1}{2.303\times2\times310}\left(200\times10^3-60\times10^3\right)$$

$$\Rightarrow \quad \log_{10}\frac{k_c}{k}=98.0$$

$$\Rightarrow \quad \frac{k_c}{k}=10^{98}$$

Note : Decrease in the activation energy in forward and backward direction by the addition of catalyst is same. i.e. $(E_a)_f-(E_{ac})_f=(E_a)_b-(E_{ac})_b$ .Thus rate constant in forward and backward directions increases by same factor. Since, for a reaction $A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B : K_{eq}=\frac{k_f}{k_b}$, adding catalyst will not alter K_{eq} of the reaction.

IN-CHAPTER EXERCISE - B

1. *Show that for a first order reaction, the time required to complete* 99.9 % *of the reaction is* 10 *times that required for the half of the reaction.*

FACTORS AFFECTING RATE OF REACTIONS

Factors affecting Rate of Reactions

The rate of reaction depends upon following factors :

1. Concentration :

In general the rate of a reaction is directly proportional to the concentration of reactants, i.e., the rate increases as the concentration of reactant(s) increases. For gaseous reaction, rate is proportional to the *partial pressures* of reactant(s).

2. Nature of Reactants :

- The rate of reactions in which complex molecules are taking part is slower than those in which simple molecules take part. A chemical reaction involves the rearrangement of atoms (i.e., breaking and reforming of bonds), hence the rearrangement of molecules involving many bonds is rather slow process and consequently the rate of a reaction is slower.
- Physical state of reactants also play key role in determining reaction rates. The greater is the surface area of a solid surface, the faster is the rate of reaction involving solid molecules. For example, the burning of wood is slower than the burning of a pulverized wood (due to increased surface area).

3. Effect of Catalyst :

The catalyst in general enhances the rate of reactions with out actually taking part in the reaction. The catalyst is used up during the reaction but at the end of reaction it is recovered as such. The phenomenon of increase in the rate of a reaction with the help of a catalyst is known as *catalysis*. Catalysts generally lower the activation energy which enables more reacting molecules to cross the energy barrier and hence increased rate of reaction.

4. Effect of Temperature :

The rate of a reaction increases by increasing the temperature. It is quite clear from Arrhenius equation $\left(k = A\,e^{-E_a/RT}\right)$, that for small rise in temperature rate of reaction increases tremendously (increase in exponential). In fact it is one of most significant factors that affects the rate most strongly. *A 10°C rise in temperature, for most of the reactions, doubles the rate of reaction.* On increasing the temperature, the number of molecules possessing activation energy increases (i.e, effective collisions) by a large quantity, as compared to the total increase in molecular collisions.

RADIOACTIVE DECAY

It is a process in which an unstable nucleus spontaneously looses energy by emitting ionizing particles and radiation. This decay results in an atom of one type (called the parent nuclide) transforming to an atom of a different type (called the daughter nuclide). This is a stochastic (random) process i.e. it is impossible to predict when a given atom will decay, but if a large number of similar atoms are given, the decay rate is predictable. The substances which undego radioactivity are called as radioactive substance. It was discovered by Henry Becquerel for atoms of Uranium. Later it was discovered that many naturally occurring compounds of heavy elements like radium, thorium etc also emit radiations. At present, it is known that all the naturally occurring elements having atomic number greater than 82 are radioactive. e.g. radium, polonium, thorium, actinium, uranium, radon etc.

The *S.I.* unit of activity is becqueral (*B.q*). One *Bq* is defined as one decay per second. Other unit of acticvity is Curic (*Ci*) and is related to *Bq* as : 1 *Ci* $= 3.7 \times 10^{10}\, Bq$

Type of decay :

Following are the decay generally occurring in nature :

(i) $\alpha -$ **decay :** In this decay, a helium nucleus $({}^4_2He)$ is emitted.

$\alpha -$ particles are He nuclei. they carry a charge of $+2e$ and mass equal to (roughly) $4m_p$. They have less penetrating power but high ionizing power and they can be deflected by electric and magnetic fields.

An $\alpha -$ decay is represented as :

$$\underset{\text{Parent nucleus}}{{}^A_ZX} \rightarrow \underset{\text{Daughter nucleus}}{{}^{A-4}_{Z-2}Y} + {}^4_2He \quad (\alpha - \text{particle})$$

e.g. $${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^4_2He$$

If the above reaction is spontaneous i.e. Q-value (or disintegration energy) is positive, it can also be represented as :

$${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^4_2He + Q$$

where $$Q = \left(m_{{}^{238}_{92}U} - m_{{}^{238}_{90}Th} - m_{{}^4_2He}\right) \times 931.5 \; MeV$$

and $m_{{}^A_ZX}$ represents mass of the nuclide ${}^A_ZX$ in amu (or μ)

(ii) $\beta -$ **decay :** In this decay, a nucleus spontaneously by emitting an electron (e^-) or a positron ($e^+ \equiv$ mass equal to m_{e^-} and charge +*e*). They can be deflected by electric and magnetic fields. They have low ionising power but high penetrating power.

Type of β decay :

(a) β^- **decay :** An $e^-\left({}^{\;0}_{-1}e\right)$ is emitted by the nucleus as :

$${}^A_Z X \rightarrow {}^{A}_{Z+1} Y + {}^{\;0}_{-1} e + \overline{v} \text{ (anti– neutrino)}$$

In this decay, a proton transforms into a neutron within the nucleus emitting a e^- :

$${}^1_o n \rightarrow {}^1_1 p + {}^{\;0}_{-1} e + \overline{v}$$

e.g. $${}^{32}_{15} p \rightarrow {}^{32}_{16} S + {}^{\;0}_{-1} e + \overline{v}$$

(b) β^+ **decay :** A positron $\left(e^+ \equiv {}^0_1 e\right)$ is emitted by the nucleus as :

$${}^A_Z X \rightarrow {}^{A}_{Z-1} Y + {}^0_1 e + v\text{(neutrino)}$$

In this decay, a proton transforms into a neutron within the nucleus emitting a e^+ :

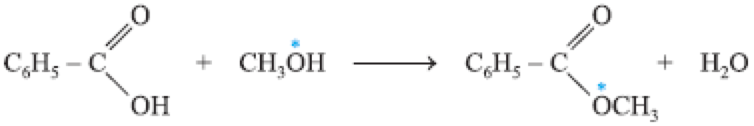
$${}^1_1 p \rightarrow {}^1_0 n + {}^0_1 e + v$$

The symbols v and $\overline{v}$ represents neutrino and anti-neutrino, these are neutral particles with zero rest mass they travel with speed of light, and they very weakly interact with matter.

Application of Radioactivity and Radioisotopes :

Radioisotopes find numerons uses in different areas. Some important applications of radioisotopes are as follows :

(i) **Tracers :** By incorporating a small amount of a radioisotope in a reaction system, one can trace the course of the reaction. Such a sample of radioisotope is called tracer. Since all the isotopes of an element are chemically equivalent, the monitored path of the isotope will indicate the path of the reaction. Consider the following esterification reaction :



By labelling the oxygen atom of methanol with ^{18}O and then using it in the esterification, it can be proved that the starred oxygen comes from the alcohol and not from the acid as the ester is found enriched with ^{18}O isotope. The use of ^{14}C as a radioactive tracer using labelled compound is well known. The dynamic nature of chemical equilibria has been established by the use of labelled compounds.

(ii) **Age of Minerals Rocks :** It involve determination of either a spaces formed during a radioactive decay or of the residual activity of an isotope which is undergoing decay. The former may be illustrated by helium dating. Helium present in uranium mineral has almost certainly been formed from α – particles.

A gram of uranium in equilibrium with its decay products produces approximately 10^{-7} g of helium per year. So if the helium and uranium contests of a mineral are known, the age of the mineral can be estimated.

The lather can be illustrated by considering a rock containing $^{238}_{92}\mathrm{U}$ which has a half life of 4.5×10^{9} years. We have seen that in the uranium decay series, $^{238}_{92}\mathrm{U}$ after a series of decay give the stable isotope $^{206}_{82}\mathrm{Pb}$ as the end product. Asuming that initially the rock did not contain any lead, we can determine the age of the rock by measuring the ratio of $^{238}_{92}U$ and $^{206}_{82}\mathrm{Pb}$ and using the equation :

$$N_t = N_0 e^{-kt}$$

where N_0 and N_t are the amounts of uranium present initially (t = 0) and after the lapse of time t, respectively and k is the decay constant.

(iii) **Radiocarbon Dating :** Radiocarbon $(^{14}_{6}C)$ dating of historical wooden derived objects is based on knowledge that the cosmic ray intensity has been practically constant for thousands of years.

$^{14}_{6}C$ is formed in the upper atmosphere by the action of cosmic radiation on

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{N} \rightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H}$$

The $^{14}\mathrm{C}$ so produced is eventually converted into carbon dioxide, which is turn is incorporated into plants and trees by the process of photosynthesis and then finds way into animals which eat plants. Because of the natural plant-animal cycle, an equilibrium is set up and all living matter contains the same small proportion of as it contains the same small proportion of as it occurs in the atmosphere. Once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of in the dead begins to fall due to the decay which undergoes.

$$^{14}_{6}C + ^{14}_{7}n \rightarrow ^{0}_{-1}\beta^{-}$$

The half life $(t_{1/2})$ period of $^{14}\mathrm{C}$ is 5770 years. A comparison of the β^{-} - activity of the dead matter with that of the carbon still in circulation enables measurement of the period of isolation of the material from the living cycle. The method, however, ceases to be accurate over period longer than two or three half life periods of $^{14}\mathrm{C}$. The proportion of $^{14}\mathrm{C}$ to $^{12}\mathrm{C}$ in living matter $1:10^{12}$.

Illustration - 8 *The beta activity of* 1g *of carbon made from green wood is* 15.3 *counts per minute. If the activity of* 1 *g of carbon derived from the wood of an Egyption mummy case is* 9.4 *counts per minute the same conditions, how old is the wood of the mummy case ?*

SOLUTION :

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = 1.20 \times 10^{-4}\ \mathrm{yr}^{-1}$$

$$\log \frac{N_0}{N_t} = \frac{kt}{2.303}$$

$$\frac{1.20 \times 10^{-4} \times t}{2.303} = \log \frac{N_0}{N_t} = \log \frac{15.3}{9.4}$$

$$\text{Hence } t = \frac{2.303}{1.20 \times 10^{-4}} \log \frac{15.3}{9.4}$$

$$t = 3920 \text{ years}.$$

Illustration - 9 *One of the hazards of nuclear explosion is the generation of* Sr^{90} *and its subsequent incorporation in bones. This nuclide has a half life of* 28.1 *year. Suppose one microgram was absorbed by a new born child, how much* Sr^{90} *will remain in his bones after* 20 years.

SOLUTION :

Given $t_{1/2} = 28.1\,\text{year}, m_{\circ} = 10^{-6}\ \text{g},\ t = 20\,\text{year}, m = ?$

$$\therefore \qquad t = \frac{2.303}{\lambda} \log \frac{m_{\circ}}{m}$$

$$\therefore \qquad 20 = \frac{2.303 \times 28.1}{0.693} \log \frac{10^{-6}}{m}$$

$$\therefore \qquad m = 6.1 \times 10^{-7}\ \text{g}$$

Illustration - 10 0.1 *g atom of radioactive isotope* ${}_{Z}X^{A}$ (*half-life* 5 *days*) *is taken. How many number of atoms will decay during eleventh day?*

SOLUTION :

$N_{\circ} = 0.1$ g atom and $t = 10$ days and $t_{1/2} = 5$ days

$$\lambda = \frac{2.303}{t}\log\frac{N_{o}}{N} \quad \Rightarrow \quad \frac{0.693}{5} = \frac{2.303}{10}\log\frac{0.1}{N}$$

$\therefore$ Amount left after 10 days $= 0.0250$ g atom

Similarly if t = 11 days

$$\frac{0.693}{5} = \frac{2.303}{11}\log\frac{0.1}{N}$$

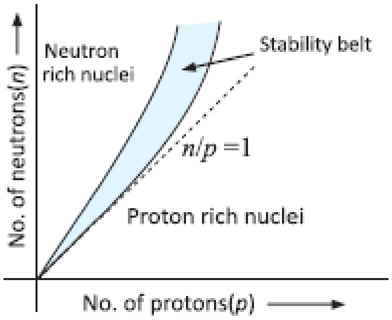
$\therefore$ Amount left after 11 days = 0.0218 g atom

$\therefore$ Amount decayed in 11 day $= 0.0250 - 0.0218$

$$= 3.2 \times 10^{-3}\text{ g atoms}$$

$$= 3.2 \times 6.023 \times 10^{23} \times 10^{-3}\text{ atoms } = 1.93 \times 10^{21}\text{ atoms}$$

Nuclear Stability :



- It has been found out that for a nuclei to be stable ratio of neutrons to protons (*n/p* ratio) should lie in the range 1 to 1.5.
- On plotting the graph of no. of neutrons to no. of protons, the stable nuclei lie in a well defined belt, called stability belt.
- The nuclei with atomic number upto 20 (Z = 20, *n* = 20 *i.e.* upto $^{40}_{20}\text{Ca}$) have *n/p* ratio close to 1 *i.e.* plot is linear with slope equal to $45°$. With increase in atomic number, the graph becomes curved whose slope increases gradually. Which means that as no. of protons increase, more no. of neutrons are required to held them together.
- The nuclei with *n/p* ratio lying above or below the stability belt are unstable. They undergo positron emission or K-capture or lose α or β – particles so that their *n/p* ratio falls within the stability belt.
- With increase in atomic number beyond 20, a nuclide (below the stability belt) decays by β^{+} – emission or *K*-electron capture so that *n/p* ratio increase to $\frac{(N+1)}{(Z-1)}$ so as to go up into the stability belt.
- Above the stability belt, the nuclide being neutron-rich decays by β^{-}, emission so that *n/p* ratio decreases to $\frac{(N-1)}{(Z+1)}$ so as to come down into the stability belt.

- When the atomic number increases beyond 82, the stability is attained by $\alpha -$ emission. The greater importance of this emission lies in the fact that number of protons decreases and so the proton-proton repulsion decrease.
  Hence the stability increases.

Note :

- It has been observed that the maximum number of stable nuclei are those which contain even number of protons and even number of neutrons. The remaining stable nuclei contain either odd number of protons or odd number of neutrons. The number of stable nuclei containing odd number of protons and odd number of neutrons is the least.
  e.g. there are only 4 nuclei (H, Li, B and N) having odd number of both protons and neutrons.

No. of n	No. of p	No. of such nuclei
even	even	160
even	odd	56
odd	even	52
odd	odd	4

- A free neutron is unstable. However, a neutron is stable inside a nucleus due to the presence of protons. Protons exert a repulsive force on each other and they need a "glue" to stay together in a nucleus which is provided by neutrons through nuclear force.

Nuclear Fission & Fusion :

(a) Nuclear Fission

The breaking of a heavy nucleus into two or more fragments of comparable masses, with the release of tremendous energy is called as nuclear fission. The most typical fission reaction occurs when slow moving neutrons strike ${}_{92}U^{235}$. The following nuclear reaction takes place :

$${}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 3\,{}_{0}n^{1} + 200MeV$$

- If more than one of the neutrons produced in the above fission reaction are capable of inducing a fission reaction (provided U^{235} is available), then the number of fissions taking place at successive stages goes increasing at a very brisk rate and this generates a series of fissions. This is known as chain reaction. The chain reaction takes place only if the size of the fissionable material (U^{235}) is greater than a certain size called the critical size.
- It the number of fission is a given interval of time goes on increasing continuously, then a condition of explosion is created. In such cases, the chain reaction is known as uncontrolled chain reaction. The forms the basis of atomic bomb.

- In a chain reaction, the fast moving neutrons are absorbed by certain substances known as moderators (like heavy water), then the number of fissions can be controlled and the chain reaction is such cases is known as controlled chain reaction. This forms the basis of a nuclear reactor.

(b) Nuclear Fusion

The process in which two or more light nuclei are combined into a single nucleus with the release of tremendous amount of energy is called as nuclear fusion. Like a fission reaction, the sum of masses before the fusion (i.e. of light nuclei) is more than the sum of masses after the fusion (i.e. of bigger nucleus) and this difference appears as the fusion energy. The most typical fusion reaction is the fusion of two deuterium nuclei into helium.

$$_1H^2 + _1H^2 \rightarrow _2He^4 + 21.6\,MeV$$

For the fusion reaction to occur, the light nuclei are brought closer to each other (with a distance of $10^{-14}m$). This is possible only at very high temperature to counter the repulsive force between nuclei. Due to the is reason, the fusion reaction is very difficult to perform. The inner core of sun is at very high temperature, and is suitable for fusion, In fact the source of sun's and other start's energy is the nuclear fusion reaction.

Laws of Radioactive Decay :

The laws of Radioactive decay are as follows :

- The disintegration of a radioactive substance is random and spontaneous.
- Radioactive decay is purely a nuclear phenomenon and is independent of any physical and chemical conditions.
- The radioactive decay follows first order kinetics, i.e., the rate of decay is proportional to the number of undecayed nuclei in a radioactive substance at any time t. If *d/N* be the number of nuclei disintegrating in time *dt*, the rate of decay is given as $\frac{dN}{dt}$.

From first order kinetic rate law : $\frac{dN}{dt} = -\lambda N$

where λ is called as decay or disintegration constant.

Rate of decay (R) i.e. Number of nuclei decaying per unit time is defined as $-\frac{dN}{dt}$

$$\Rightarrow \qquad R(t) = -\frac{dN}{dt}$$

Let N_0 be the number of nuclei at time t = 0 and N_t be the number of nuclei after time t, then according to integrated first order rate law, we have:

$$N_t = N_0 e^{-\lambda t}$$

$\Rightarrow \quad \lambda t = \ell n \dfrac{N_0}{N_t} = 2.303 \ell og \dfrac{N_0}{N_t}$ and $\quad R(t) = \lambda N_0 e^{-\lambda t} = \lambda N$ where R_0 is the decay rate at $t = 0$

- The half life $(t_{1/2})$ period of a radioactive substance is defined as the time in which one-half of the radioactive substance is disintegrated. If N_0 be the number of nuclei at $t = 0$, then in a half life $t_{1/2}$, the number of nuclei decayed will be N_0.

$$N_t = N_0 e^{-\lambda t} \qquad \textbf{...(i)} \qquad \Rightarrow \qquad \frac{N_0}{2} = N_0 e^{-\lambda t_{1/2}} \qquad \textbf{...(ii)}$$

From **(i)** and **(ii)** $\dfrac{N_t}{N_0} = \left(\dfrac{1}{2}\right)^n$ n: number of half lives $= \dfrac{t}{t_{1/2}}$

The half life $(t_{1/2})$ and decay constant (λ) are related as : $t_{1/2} = \dfrac{0.693}{\lambda}$

- The mean life (τ) of a radioactive substance is equal to the sum of life times of all atoms divided by the number of all nuclei and can be calculated as follows :
  No. of nuclei decaying between time t and $t + dt$ are equal to $dN = R(t)\, dt$

$$\Rightarrow \qquad dN = \lambda N_0 e^{-\lambda t} dt$$

The life of these nuclei is thus $= \lambda N_0 e^{-\lambda t} dt \times t$

$$\Rightarrow \qquad \text{Average life } (\tau) = \frac{\text{Total life of all nuclei}}{\text{Total nuclei}} \qquad \Rightarrow \qquad \tau = \frac{\int_0^{\infty} \lambda t N_0 e^{-\lambda t} dt}{N_0} = \frac{1}{\lambda}$$

Illustration - 11 *At a given instant there are* 25% *undecayed radio-active nuclei in a sample. After* 10 *seconds the number of undecayed nuclei reduces to* 12.5% *Calculate* (i) *mean-life of the nuclei, and* (ii) *the time in which the number of undecayed nuclei will further reduce to* 6.25%.

SOLUTION :

$$25.0\% \rightarrow 12.5\%$$

$\Rightarrow$ time taken is one half life $\Rightarrow$ $t_{1/2} = 10\,\text{sec}$ or $\lambda = \dfrac{0.693}{t_{1/2}}$ or $\tau = \dfrac{1}{\lambda} = 0.1\,\text{sec}$

$$12.5\% \rightarrow 6.25\%$$

$\Rightarrow$ time taken is one half life $\Rightarrow$ $t = 10\,\text{sec}$

Illustration - 12 *A radioactive sample of* ^{238}U *decays to Pb through a process for which the half-life is* 4.5×10^9 *years. Find the ratio of number of nuclei of the Pb to* ^{238}U *after a time of* 1.5×10^9 *years. Given* $(2)^{1/3}=1.26.$

SOLUTION :

$$\frac{N_t}{N_0}=\left(\frac{1}{2}\right)^n \text{ where } n=\frac{t}{t_{1/2}}=\frac{1.5\times10^9}{4.5\times10^9}=\frac{1}{3}$$

$$\Rightarrow \quad \frac{N_t}{N_0}=\left(\frac{1}{2}\right)^{1/3}=\frac{1}{1.26}$$

$$\begin{array}{lcc} & ^{238}U & \rightarrow Pb \\ t=0 & x & - \\ t=t & x-y & y \end{array}$$

$$\Rightarrow \quad \frac{x}{x-y}=1.26 \qquad \Rightarrow \quad \frac{y}{x-y}=\frac{(N_t)_{Pb}}{(N_t)_U}=0.26$$

Illustration - 13 $_{84}Po^{210}$ *decays with a-particle to* $_{82}Pb^{206}$ *with a half life of* 138.4 *days. If* 1.0 *g of* $_{84}Po^{210}$ *is placed in a sealed tube, how much helium will accumulate in* 69.2 *days ? Express the answer in* cm^3 *at* STP.

SOLUTION :

$t_{1/2}=138.4$ days, $t=69.2$ *days*

$\therefore$ No. of half-lives $n=\dfrac{t}{t_{1/2}}=\dfrac{69.2}{138.4}=\dfrac{1}{2}$

$\therefore$ Amount of Po left after 69.2 days $=\dfrac{1}{(2)^{1/2}}g=0.707\,g$

$\therefore$ Amount of Po used in 69.2 days $=1-0.707=0.293g$

$\therefore$ Now $_{84}Po^{210}\rightarrow {}_{82}Pb^{206}+{}_2He^4$

$\therefore$ 210 g Po on decay will produce = 4 g He

$\therefore$ 0.293 g Po decay will produce $=\dfrac{4\times0.293}{210}=5.581\times10^{-3}$ g He

$\therefore$ Volume of He at STP $=\dfrac{5.581\times10^{-3}\times22400}{4}=31.25\,cm^3$

Illustration - 14 *In nature a decay chain series starts with* $_{90}Th^{232}$ *and finally terminates at* $_{82}Pb^{208}$. *A thorium ore sample was found to contain* $8\times10^{-5}\,ml$ *of He at STP and* $5\times10^{-7}\,g$ *of* Th^{232}. *Find the age of ore sample assuming that source of He to be only due to decay of* Th^{232}. *Also assume complete retention of He with in the ore.* $[t_{1/2}$ *of* $Th^{232} = 1.39\times10^{10}$ *years*$]$.

SOLUTION :

$$_{90}Th^{232} \rightarrow {}_{82}Pb^{208} + 6\,{}_2He^4 + 4\,{}_{-1}e^0$$

$\therefore$ $6\times22400\,ml$ He is formed by 232 g thorium decay

$\therefore$ $8\times10^{-8}\,ml$ He is formed by $= \dfrac{232\times8\times10^{-5}}{6\times22400}\,g$ thorium decay $= 1.38\times10^{-7}\,g$

After time t, amount of thorium $= 5\times10^{-7}\,g$

At t = 0, amount of thorium in the sample $= 5\times10^{-7} + 1.38\times10^{-7} = 6.38\times10^{-7}\,g$

$$\text{Now, } t = \frac{2.303}{\lambda}\log\frac{m_\circ}{m} = \frac{2.303\times1.39\times10^{10}}{0.693}\log\frac{6.38\times10^{-7}}{5\times10^{-7}} = 4.89\times10^{9}\text{ years}$$

Illustration - 15 *An experiment requires minimum* β *activity produced at the rate of* 346 $\beta-$ *particles per minute. The half life period of* $_{42}Mo^{99}$ *which is a* β *emitter is 66.6 hrs. Find the minimum amount of* $_{42}Mo^{99}$ *required to carry out the experiment in* 6.909 *hours.*

SOLUTION :

To carry out experiment, Activity at the last minute of 6.909th hour = 346 dpm.

$$\text{Now, } t = \frac{2.303}{\lambda}\log\frac{A_\circ}{A_t}$$

$$6.909 = \frac{2.303\times66.6}{0.693}\log\left(\frac{A_\circ}{346}\right)$$

$$\log\left(\frac{A_\circ}{346}\right) = \frac{6.909\times0.693}{2.303\times66.6} = 0.03121$$

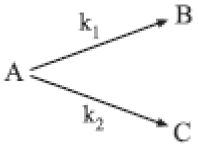
$\therefore$ $A_\circ = 346\times1.0745 = 371.77$

$$\text{Now, } A_\circ = \lambda N_\circ \quad\Rightarrow\quad N_\circ = \frac{371.77}{0.693}\times66.6\times60 = 35728.5\times60 = 2143710$$

Amount of Mo required to carry out experiment in 6.909 hour $= \dfrac{99}{6.023\times10^{23}}\times2143710 = 3.52\times10^{-16}\,g$

ADVANCED KINETICS Section - 7

1. Parallel / Side Reactions (Elementary Reactions) :



Rate of consumption of 'A' in $A \longrightarrow B : \left.\frac{d[A]}{dt}\right|_1 = -k_1[A]$ $\left[\because \text{Rate of Reaction} = k_1[A] = -\left.\frac{d[A]}{dt}\right|_1\right]$

Similarly, Rate of consumption of 'A' in $A \longrightarrow C : \left.\frac{d[A]}{dt}\right|_2 = -k_2[A]$

⇒ Overall (net) rate of consumption of 'A' = $\frac{d[A]}{dt} = \left.\frac{d[A]}{dt}\right|_1 + \left.\frac{d[A]}{dt}\right|_2 = -k_1[A] - k_2[A]$

⇒ $\frac{d[A]}{dt} = -(k_1 + k_2)[A] = -k_{overall}[A]$ **. . . . (i)**

⇒ The Overall reaction is also of the same order (here, I^{st} order) with $k_{overall} = k_1 + k_2$

Check yourself that solution of (i) is :

$$\boxed{[A] = [A]_0\, e^{-(k_1+k_2)t}}$$

Also, from the rate equation : $\frac{d[B]}{dt} = +k_1[A]$ and $\frac{d[C]}{dt} = +k_2[A]$

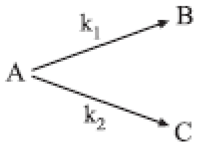
Substituting the value of [A] (t) in the differential equation for [B] and [C] and integrating, we get :

$$[B] = [B]_o + \int_0^t k_1[A]_0 e^{-(k_1+k_2)t}\, dt = [B]_0 + \frac{k_1[A]}{(k_1+k_2)}\left(1 - e^{-(k_1+k_2)t}\right)$$

and $$[C] = [C]_o + \int_0^t k_2[A]_0 e^{-(k_1+k_2)t}\, dt = [C]_0 + \frac{k_2[A]}{(k_1+k_2)}\left(1 - e^{-(k_1+k_2)t}\right)$$

Also, if $[B]_0$ and $[C]_0 = 0$, we get : $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

Illustrating the concept :



$k_1 = 10^{-3}s^{-1}$ *and* $k_2 = 2 \times 10^{-3}s^{-1}$. *Find the overall half life of the reaction.*

SOLUTION :

$$k_{overall} = k_1 + k_2 = 3 \times 10^{-3}s^{-1}$$

$$t_{1/2} = \frac{0.693}{k_{overall}} = \frac{0.693}{3\times10^{-3}}s = 231\,sec.$$ [Note : Reactions are of first order].

2. Consecutive Reactions (Elementary Reactions) :

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\frac{d[A]}{dt} = -k_1[A] \qquad \text{....(i)}$$

$$\frac{d[B]}{dt} = +k_1[A] - k_2[B] \qquad \text{....(ii)}$$

$$\frac{d[C]}{dt} = +k_2[B] \qquad \text{....(iii)}$$

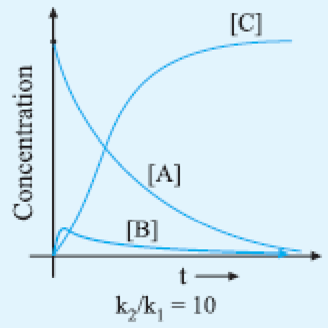
On solving the above differential equations, we get :

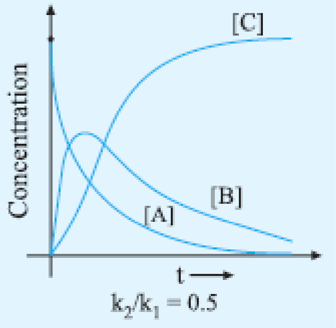
$$[A] = [A]_0\, e^{-k_1t} \qquad \text{....(iv)}$$

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1}\left(e^{-k_1t} - e^{-k_2t}\right) \qquad \text{....(v)}$$

$$[C] = [A]_0\left(1 + \frac{k_1e^{-k_2t} - k_2e^{-k_1t}}{k_2 - k_1}\right) \qquad \text{....(vi)}$$

Note : ➤ $[A] + [B] + [C] = [A]_0$ [Assuming $[B]_0 = [C]_0 = 0$]





- [B] is maximum when $\frac{d[B]}{dt}=0$

$\Rightarrow$ $k_1[A] = k_2\,[B]_{max.}$ **. . . . (vii)**

Using (v), $\frac{d[B]}{dt}=-k_1e^{-k_1t}+k_2e^{-k_2t}=0 \Rightarrow k_1e^{-k_1t}=k_2e^{-k_2t}$

$\Rightarrow$ $t=\frac{1}{k_2-k_1}\ell n\frac{k_2}{k_1}$

Thus, at $t=\frac{1}{k_2-k_1}\ell n\frac{k_2}{k_1}$, [B] is maximum.

Illustration - 16

$$A\xrightarrow{k_1=0.1s^{-1}}B\xrightarrow{k_2=1/30s^{-1}}C$$

Find the time at which concentration of B is maximum. Also, find the concentration of A, B, and C at this instant. Take $[A]_0 = 1M$

SOLUTION :

[B] is maximum at $t=\frac{1}{k_2-k_1}\ell n\frac{k_2}{k_1}=\frac{1}{0.1-1/30}\ell n\frac{0.1}{1/30}=15\,\ell n\,3$ sec.

$$[A]_{t=15\,\ell n3}=[A]_0\,e^{-k_1t}$$

$$=1\times e^{-0.1\times15\ell n3}=e^{\ell n(3^{-1.5})}=3^{-1.5}=\frac{1}{3\sqrt{3}}M$$

When [B] is max : $k_1[A]=k_2\,[B]_{max.}\left(\frac{d[B]}{dt}=0\right)$

$\Rightarrow$ $\frac{1}{10}\times\frac{1}{3\sqrt{3}}=\frac{1}{30}[B]_{max.}$ $\Rightarrow$ $[B]_{max.}=\frac{1}{\sqrt{3}}M$

Also, $[A]+[B]+[C]=[A]_0$

$$[C]=1-\frac{1}{3\sqrt{3}}-\frac{1}{\sqrt{3}}=1-\frac{4}{3\sqrt{3}}M$$

3. Reversible Reaction (Elementary Reactions) :

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Net rate of consumption of 'A' $= \frac{d[A]}{dt} = -k_1[A] + k_2[B]$

Also, $[A] + [B] = [A]_0 \quad \Rightarrow \quad [B] = [A]_0 - [A]$

$$\Rightarrow \quad \frac{d[A]}{dt} = -k_1[A] + k_2([A]_0 - [A])$$

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] + k_2[A]_0$$

At equilibrium, $\frac{d[A]}{dt} = 0 \quad \Rightarrow \quad k_1[A]_{eq} = k_2[B]_{eq}$

$$\Rightarrow \quad K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_2}$$

Try yourself : Find $[A]_t = ?$ and $[B]_t = ?$

SUBJECTIVE SOLVED EXAMPLES

Example - 1 *The vapour pressure of two miscible liquids 'A' and 'B' are 300 and 500 mm of Hg respectively. In a flask, 10 mol of 'A' is mixed with 12 mol of 'B'. However, as soon as 'B' is added, 'A' starts polymerising into a completely insoluble solid. This polymerisation follows first-order kinetics. After 100 minutes, 0.525 mol of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution.*

[*Given*, $\log_{10} 11 = 1.04$]

SOLUTION :

We have :

$P_A^0 = 300$ mm Hg and $P_B^0 = 500$ mm Hg

$n_{A0} = 10$ mol and $n_{B0} = 12$ mol

Let the amount of A after 100 min is reduced to n_A.

At this stage :

$$n_{Total} = n_A + n_B + n_{Solute} = n_A + 12 + 0.525$$

Mole fractions of A and B in the solution will be

$$\chi_A = \frac{n_A}{n_A + 12.525} \text{ and } \chi_B = \frac{12}{n_A + 12.525}$$

Since $P_{Total} = P_A^0 \chi_A = P_B^0 \chi_B$, , we get

$$400 = 300 \times \frac{n_A}{n_A + 12.525} + 500 \times \frac{12}{n_A + 12.525}$$

Solving for n_A, we get :

$$n_A = 9.90 \text{ mol}$$

$$nA \longrightarrow A_n$$

For the first-order kinetics, we have :

$$kt = 2.303 \log_{10} \frac{[A]_0}{[A]_t}$$

or $$k(100 \text{ min}) = 2.303 \log_{10} \frac{10}{9.9}$$

$\Rightarrow$ $k = 1.00 \times 10^{-4}$ min^{-1} $= 1.67 \times 10^{-6}$ s^{-1}

Example - 2 *A first order reaction :* $A \longrightarrow B$ *requires activation energy of* 89 *kJ/mol. When* 20% *solution of A was kept at* 27°C *for* 40 *minutes,* 25% *decomposition took place. What will be the percent decomposition in the same time in a* 30% *solution maintained at* 37°C ? *Assume that the activation energy remains constant in this range of temperature.*

SOLUTION :

Note : It does not atter whether you take 20%, 30%, 40% or 70% of ‘A’ because first order reaction is independent of the initial concentration of reactant.

At 27°C, 20% of A decomposes 25%

$$\Rightarrow \quad kt = 2.303 \log_{10}\frac{C_0}{C_t} = 2.303 \ \log_{10}\frac{1}{1-\alpha} = \ell n\frac{1}{1-\alpha} \ [\alpha = 0.25]$$

$$\Rightarrow \quad k(40) = \ell n\frac{100}{75}$$

$$\Rightarrow \quad k \text{ (at 300 K)} = \frac{1}{40}\ell n\frac{4}{3}\text{min}^{-1}$$

Using Arrhenius equation find k at 310K.

$$\log_{10}\frac{k_{310}}{k_{300}} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log_{10}\frac{k_{310}}{k_{300}} = \frac{89\times10^3}{2.303\times8.31}\left(\frac{310-300}{300\times310}\right) = 0.5$$

$$\Rightarrow \quad k(\text{at 310 K}) = k(\text{at 300K}) \times \sqrt{10}$$

Now calculate % decomposition at 310K using first order kinetics.

$$kt = 2.303 \log_{10}\frac{C_0}{C_t}$$

$$\Rightarrow \quad k \times 40 = \ell n\frac{1}{1-\alpha}$$

$$\Rightarrow \quad \ell n\frac{1}{1-\alpha} = \left[\left(\frac{1}{40}\ \ell n\frac{4}{3}\right)\times\sqrt{10}\right]\times 40 = 0.91$$

$$\Rightarrow \quad \log_{10}\frac{1}{1-\alpha} = \frac{0.91}{2.303} = 0.40$$

$$\frac{1}{1-\alpha} \approx 2.5 \quad \Rightarrow \quad \alpha = 0.6$$

$$\Rightarrow \quad \alpha = 0.6 \equiv 60.0\ \%\ \text{decomposition of A at 310 K.}$$

Example - 3 *A certain reaction A + B ⟶ products ; is first order w.r.t. each reactant with* $k = 5.0 \times 10^{-3}\ M^{-1}s^{-1}$. *Calculate the concentration of A remaining after 100s if the initial concentration of A was 0.1 M and that of B was 6.0 M. State any approximation made in obtaining your result.*

SOLUTION :

$$A + B \longrightarrow \text{products}$$

Given : Rate = k [A][B] (2^{nd} Order reaction)

Now, since [B] >> [A], [B] can be assumed to remain constant throughout the reaction. Thus, the rate law for the reaction, becomes :

Rate ≈ k_0 [A]

where $k_0 = k\,[B] = 5.0 \times 10^{-3} \times 6.0\ s^{-1}$

$= 3.0 \times 10^{-2}\ s^{-1}$

Thus, the reaction is now of first order [Pseudo first order].

Note :

	A	+	B	$\xrightarrow{k}$	products
	0.1M		6.0M		
	$0.1 - x$		$6.0 - x$		

Using, $2.303 \log_{10}\dfrac{C_{0A}}{C_{tA}} = k_0 t$

$$\Rightarrow \quad 2.303 \log_{10}\frac{0.1}{C_{tA}} = k_0 t = 3$$

$$\Rightarrow \quad \log_e \frac{0.1}{C_{tA}} = 3$$

$[\because \log_e x = 2.303 \log_{10} x]$

$$\Rightarrow \quad C_{tA} = 10e^{-3} = 5 \times 10^{-3} M$$

Check your approximation :

$[B]_{change} = x = 0.1 - 5 \times 10^{-3}$

$= 0.095$ M

$$\%\ [B]_{change} = \frac{0.095}{6} \times 100\% = 1.58\%$$

Example - 4 *The gas phase decomposition of* N_2O_5 *to* NO_2 *and* O_2 *is monitored by measurement of total pressure. The following data are obtained.*

P_{total} (atm)	0.154	0.215	0.260	0.315	0.346
Time (sec)	1	52	103	205	309

Find the average rate of disappearance of N_2O_5 *for the time interval between each interval and for the total time interval. [Hint : Integrated rate law is NOT to be used].*

SOLUTION :

	$2N_2O_5\,(g)$	$\longrightarrow$	$4NO_2\,(g)$	+	$O_2\,(g)$
Initial Pressure (at t = 0)	P_0		0		0
At t = t	$P_0 - 2x$		$4x$		x

Now : $P_{Total} = (P_0 - 2x) + 4x + x \Rightarrow x = \frac{1}{3}(P_{Total} - P_0)$

$$P_{N_2O_5} = P_0 - 2x = (5P_0 - 2P_{Total}) = P_t$$

Thus, $\Delta P_{N_2O_5} = \frac{2}{3}(P_{t1} - P_{t2})$ where P_{t2} and P_{t1} are the total pressures at time instants t_2 and t_1 $(t_2 > t_1)$ respectively

P_{total} (atm)	Time (sec)	$\frac{\Delta P_{N_2O_5}}{\Delta t}$ = Avg. Rate of disappearance of N_2O_5 (atm/sec.)
0.154	1	$\frac{2}{3}\frac{(0.154-0.215)}{(52-1)} = -7.97 \times 10^{-4}$
0.215	52	$\frac{2}{3}\frac{(0.215-0.260)}{(103-52)} = -5.88 \times 10^{-4}$
0.260	103	$\frac{2}{3}\frac{(0.260-0.315)}{(205-103)} = -3.59 \times 10^{-4}$
0.315	205	$\frac{2}{3}\frac{(0.315-0.346)}{(309-205)} = -1.99 \times 10^{-4}$
0.346	309	

Example - 5 *In an ore containing Uranium, the ratio of* U^{238} *to* Pb^{206} *nuclei is* 3. *Calculate the age of the ore, assuming that all the lead present in the ore is the final stable product of* U^{238}. *The half life of* U^{238} *is* 4.5×10^9 *years.*

SOLUTION :

Note : The radio active decay follows first order kinetics. Here, we take $N_0 \equiv C_0$ and $N_t \equiv C_t$ and $\lambda \equiv k$

The first order rate equation for radioactive decay is :

$$\lambda t = 2.303 \log \frac{N_0}{N_t} \qquad \text{where } \lambda = \frac{0.693}{t_{\frac{1}{2}}}$$

N_0 = initial nuclei (at t = 0)

N_t = final nuclei (at t)

λ = decay constant or disintegration constant

$$\begin{array}{lccc} & U^{238} & \longrightarrow & Pb^{206} \\ N_0 \equiv & x & & 0 \\ N_t \equiv & x-y & & y \end{array}$$

$$\Rightarrow \frac{N_0}{N_t} = \frac{x}{x-y}$$

Using $\lambda t = 2.303 \log_{10} \dfrac{x}{x-y}$

Given : $\dfrac{x-y}{y} = 3 \qquad \Rightarrow \dfrac{x}{x-y} = \dfrac{4}{3}$

$$\Rightarrow \quad t = \frac{2.303}{0.693} \times 4.5 \times 10^9 \log_{10} \frac{4}{3}$$

$$\Rightarrow \quad t = 1.85 \times 10^9 \text{ years.}$$

Example - 6 *The nucleidic ratio of* $_1H^3$ *to* $_1H^1$ *in a sample of water is* 8.0 × 10^{-18} : 1. *Tritium undergoes decay with a half life period of* 12.0 *years. How many tritium atoms would a* 10.0 *gm of such sample contain* 36 *years after the original sample is collected* ?

SOLUTION :

The ratio of tritium atoms to that of H–atoms will be same as the ratio of moles of T-atoms to that of H–atoms, since 1 mole of $T_2O \equiv 2$ mole of T atoms and 1 mole of $H_2O \equiv 2$ mole of H atoms.

Calculate the initial number of tritium atoms.

10 gm = mass of T_2O + mass of H_2O

$$= n_{T_2O} \times 22 + n_{H_2O} \times 18$$

$$= \left(8 \times 10^{-18} n_{H_2O}\right) \times 22 + n_{H_2O} \times 18$$

$$\approx n_{H_2O} \times 18$$

$$\Rightarrow \quad n_{H_2O} = \frac{10}{18} = \frac{5}{9}$$

$$\Rightarrow \quad n_{T_2O} = \frac{5}{9} \times 8 \times 10^{-18} = \frac{40}{9} \times 10^{-18}$$

$$\Rightarrow \quad (N_T)_O = \left(N_{T_2O}\right) \times 2$$

$$= \left(\frac{40}{9} \times 10^{-18} \times 6 \times 10^{23}\right) \times 2$$

$$= 5.33 \times 10^6 \text{ atoms}$$

$$\underset{(x)}{\text{No. of half lives}} = \frac{36}{12} = 3$$

Use : $N_t = N_0 \left(\dfrac{1}{2}\right)^x = N_0 \left(\dfrac{1}{2}\right)^3$

$$= \frac{1}{8} \times 5.33 \times 10^6 \text{ atoms}$$

$$= 6.66 \times 10^5 \text{ atoms}$$

Example - 7 *Dimethyl ether decomposes according to the following reaction :*

$$CH_3-O-CH_3\,(g) \longrightarrow CH_4\,(g) + CO(g) + H_2\,(g)$$

At a certain temperature, when ether was heated in a closed vessel, the increase in pressure with time was noted down.

Time (min)	0	10	20	30
Pressure (mm Hg)	420	522	602	678

(i) *Show that the reaction is first order.* **(ii)** *Compute the pressure of CO (g) after 109 minutes.*

SOLUTION :

$$CH_3-O-CH_3\,(g) \longrightarrow CH_4\,(g) + CO\,(g) + H_2\,(g) \qquad \textit{(all are gases)}$$

time	CH_3-O-CH_3	CH_4	CO	H_2
$t = 0$	$C_0 \equiv P_0$	0	0	0
$t = t$	$C_t \equiv P_0 - x$	x	x	x

$$\Rightarrow \quad P_t = P_0 + 2x$$

$$\Rightarrow \quad x = \frac{1}{2}(P_t - P_0)$$

$$\Rightarrow \quad \frac{C_0}{C_t} = \frac{P_0}{P_0 - x} = \frac{2P_0}{3P_0 - P_t}$$

Now find k_1, k_2 and k_3 using the first order kinetics

$$kt = 2.303 \log_{10} \frac{2P_0}{3P_0 - 2P_t}$$

$$k_1 = \frac{2.303}{10} \log_{10} \frac{2(420)}{3(420) - 522} = 0.0129\ \text{min}^{-1}$$

$$k_2 = \frac{2.303}{20} \log_{10} \frac{2(420)}{3(420) - 602} = 0.0122\ \text{min}^{-1}$$

$$k_3 = \frac{2.303}{30} \log_{10} \frac{2(420)}{3(420) - 678} = 0.0123\ \text{min}^{-1}$$

As $k_1 \sim k_2 \sim k_3$, the reaction is first order.

$$k_{average} = \frac{1}{3}(k_1 + k_2 + k_3) = 0.0127\ \text{min}^{-1}$$

$$\Rightarrow \quad t_{1/2} = \frac{0.693}{k} = 54.56\ \text{min}$$

$$\text{No. of half lives} = \frac{109}{54.56} \approx 2$$

$$\Rightarrow \quad (P_t)_{CH_3OCH_3} = P_0\left(\frac{1}{2}\right)^2 = \frac{420}{4}$$

$$= 105 \text{ mm Hg} = P_0 - x$$

$$\Rightarrow \quad x = P_{CO} = 420 - 105 = 315 \text{ mm Hg}$$

Example - 8 *The decomposition of N_2O_5 according to following reaction is first order reaction :*

$$2N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$$

After 30 min. from start of the decomposition in a closed vessel, the total pressure developed is found to be 250 mm of Hg and on complete decomposition, the total pressure is 500 mm of Hg. Calculate the rate constant of the reaction.

SOLUTION :

$$\begin{array}{llll} & 2N_2O_5(g) & \longrightarrow \; 4NO_2(g) & + \; O_2(g) \\ t = 0 & P_0 & 0 & 0 \\ t = t & P_0 - 2x & 4x & x \\ t = \infty & - & 2P_0 & P_0/2 \end{array}$$

P_0 : initial presure ; Let P_t : pressure at 30 min and
P_∞ : pressure at the end of decomposition

$$\Rightarrow \quad P_t = P_0 + 3x \quad \Rightarrow \quad x = \frac{1}{3}(P_t - P_0) \qquad \text{and} \qquad P_\infty = 2P_0 + \frac{1}{2}P_0 = \frac{5}{2}P_0$$

$$\Rightarrow \quad P_0 = \frac{2}{5}P_\infty = \frac{2}{5} \times 500 = 200 \text{ mm Hg}$$

For the first order kinetics

$$kt = 2.303 \log_{10}\frac{C_0}{C_t}$$

C_0 : initial concentration ; C_t : final concentration

$$\text{Now} \quad \frac{C_0}{C_t} = \frac{P_0}{P_0 - 2x} \qquad \text{and} \qquad x = \frac{1}{2}(250 - 200) = \frac{50}{3}$$

$$\Rightarrow \quad \frac{C_0}{C_t} = \frac{200}{200 - 2 \times \frac{50}{3}} = \frac{6}{5}$$

$$\Rightarrow \quad k = \frac{1}{30} \times 2.303 \log_{10}\frac{6}{5} = 6.08 \times 10^{-3} \text{ min}^{-1}$$

THINGS TO REMEMBER

1. $mA + nB \xrightarrow{k} pC + qD$

- Rate of reaction $= k[A]^m[B]^n = -\frac{1}{m}\frac{d[A]}{dt} = -\frac{1}{n}\frac{d[B]}{dt} = +\frac{1}{p}\frac{d[C]}{dt} = +\frac{1}{q}\frac{d[D]}{dt}$

  where k depends only on T.

- Units of k = $(mol/L)^{1-n}(time)^{-1}$

2. $A \xrightarrow{k} B$

nth order reaction : Half life $(t_{1/2}) = \frac{2^{n-1}-1}{(n-1)\,kC_0^{n-1}} \Rightarrow t_{1/2} \propto \frac{1}{C_0^{n-1}}$

and $\frac{1}{(n-1)}\left[\frac{1}{C_t^{n-1}} - \frac{1}{C_0^{n-1}}\right] = kt$

3. First order reaction : $A \xrightarrow{k} B$

$$kt = 2.303\log_{10}\frac{C_0}{C_t} = 2.303\log_{10}\frac{C_0}{C_0 - x} = 2.303\log_{10}\frac{1}{1-\alpha}$$

Half life $(t_{1/2}) = \frac{0.693}{k}$ (independent of initial concentration of the reactant)

$$C_t = C_0\left(\frac{1}{2}\right)^x \quad \text{where } x = \frac{t}{t_{1/2}} = \text{No. of half lives}$$

4.
- Arrhenius Equation : $k = Ae^{-Ea/RT}$

  where A = Arrhenius factor OR Pre-exponential factor and E_a = Activation energy

- k can be increased by increasing T OR reducing E_a (addition of catalyst)

  (i) Temperature effect : $\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

  (ii) Catalyst effect : $\log_{10}\frac{k_2}{k_1} = \frac{E_a - E_{ac}}{2.303RT}$

SOLUTIONS TO IN-CHAPTER EXERCISE-B

1. $t_{99.9\%} = \frac{2.303}{k}\log_{10}\frac{C_0}{C_0 - 0.999C_0} = \frac{2.303}{k}\log_{10}1000 = \frac{3 \times 2.303}{k}$

$t_{1/2} = \frac{2.303\log_{10}2}{k} \Rightarrow \frac{t_{99.9\%}}{t_{1/2}} = \frac{3}{\log_{10}2} \approx 10$